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FINAL REPORT

Grant #: N00014-00-1-0108

Principal Investigator: Dr. Charles R. Martin

Institution: University of Florida

Grant Title: Nanotubule Membranes - Fundamentals and Applications in Electrochemical Energy and Stochastic Sensing

Award Period: 15 Nov 1999 to 14 Nov 2002

Objective: The objectives are: 1) To develop the measurement technology that will allow us to determine if the α -hemolysin channel has been successfully immobilized, 2) To develop ultrathin film channel immobilization technology, and 3) To develop methods for isolating a single nanotubule in an Au nanotubule membrane. For the Electrochemistry Division the objectives are 1) To develop new classes of nanotubule membranes whose transport properties can be modulated electrochemically by applying a potential to the membrane, 2) To show that surface chemistry of these nanotubule membranes can varied by simple chemical and electrochemical derivatization schemes, 3) To study electroosmotic flow phenomena in these new membranes.

Approach: With funds from a previous ONR grant the P.I. has developed a procedure for preparing Au nanotubules within the pores of a microporous polycarbonate template membrane. These nanotubules have monodisperse diameters that can be controlled at will down to molecular dimensions (<1 nm). For the Biomolecular Division we want to immobilize α -hemolysin channels within these nanotubules to develop a new type of stochastic sensor that is rugged, reliable and practical. We have focused our efforts during the preceding year on two important goals. First, we are exploring methods for preparing surface films that will coat the nanotubule membrane surface and serve as the host for the α -hemolysin channel. Second, we are developing the technology for isolating a single nanotubule in such membranes. For the Electrochemistry Division we are exploring ways of electrochemically modulating transport in nanotubule membranes. We are investigating both the Au nanotubule membranes prepared by electroless deposition of Au within the pores of nanoporous polycarbonate templates and carbon nanotubule membranes prepared by chemical vapor deposition of C within the pores of microporous alumina templates. In both cases the nanotubule material is an electronic conductor. This allows us to apply a potential to the nanotubules relative to an external reference electrode immersed into a contacting electrolyte phase. It is via this route that we electrochemically modulate the transport properties of the membrane. We are electrochemically modulating both transport by diffusion and transport by electroosmotic flow across the membrane.

Accomplishments: For the Biomolecular Division our priority during previous three years was to develop a method preparation and characterization of a "bilayer mimic" on the surface of our gold nanotube membranes that will function as a host for the α -hemolysin channel. We are currently writing a research article on this new method. We have focused on the two objectives noted above - surface films and single pore membranes. In nature, the α -hemolysin channel self-assembles from solution across a lipid bilayer membrane. We need to be able to mimic this process such that the channel assembles at the surface of our nanotube membrane. Hence, the "bilayer mimic" must emulate a lipid bilayer.

The approach we are pursuing to prepare this surface film entails thiol chemisorption based on the micro-contact printing technique of the Whitesides group. By "inking" a poly(dimethylsiloxane) stamp with a desired thiol, we have been able to reproducibly transfer a stable, well-ordered monolayer to the nanotubule membrane surface. Because the key chemical characteristic of the interior of a lipid bilayer membrane is that it is hydrophobic, we have used hexadecanethiol (HDT) for the majority of these studies, and only those results will be presented here. We are currently using AC impedance and cyclic voltammetric methods, as well as contact angle measurements and transport experiments to characterize these films as we need to show that this route yields defect free ultrathin films that chemisorb only to the nanotube mouth and not along the walls of the nanotube.

The AC impedance and cyclic voltammetry data address the issue of whether or not the nanotubules are being wet when both faces are stamped. To study this, one face of the nanotubule membrane was stamped and exposed to solution while the other face was covered with a tape mask. In the voltammetry experiments, the stamped membrane was exposed to a solution of $\text{Fe}(\text{CN})_6^{3-}$. The absence of a large cathodic current indicates that the stamped HDT monolayer is not only blocking redox activity of the $\text{Fe}(\text{CN})_6^{3-}$ on the membrane face, but is also blocking it from occurring in the nanotubules by keeping the solution out of the nanotubules. In the AC impedance experiments, we were able to show that the resistance of the HDT stamped membrane decreases when exposed to a dilute solution of the anionic surfactant dodecylbenzene sulfonic acid (DBS). We have previously shown that DBS partitions into a hydrophobic monolayer, allowing the wetting of nanotubules. Through the experiments done using via these two methods, we were able to confirm that stamped monolayers effectively keep water out of the nanotubules.

We have also begun preliminary work using wild-type α -Hemolysin (α HL) provided by Dr. Hagan Bayley. In these experiments, we have been studying the interaction of α HL with the stamped monolayer by a series of contact angle measurements. We observed that the contact angle of a stamped membrane decreases significantly after exposure to α HL, suggesting that the α HL is strongly physisorbed to the HDT monolayer.

We have succeeded in etching pores of varying diameter, from $\sim 1 \mu\text{m}$ down to 30 nm, in these membranes, and we have imaged these pores with optical and electron microscopy. We have also developed a procedure based on fluorescence microscopy for isolating a single nanoscopic pore. Briefly, after etching the membrane, it is sputtered with gold to render it optically opaque. A drop of a fluorescent dye is placed on a microscope slide and the etched membrane is placed on top of the drop. The dye wicks through the pore and forms a droplet that is visible using the fluorescent microscope. A piece of Scotch tape with a punch hole is placed around the droplet, effectively isolating a single pore from neighboring pores. We are then able to verify pore diameter using scanning electron microscopy.

For the Electrochemistry Division, we have focused our efforts on the modulation of transport through carbon nanotubule membranes. Using electroosmotic flow, we have completely shut off transport across the membrane as well as enhancing it four fold. We have electrochemically modified the surface chemistry of the carbon nanotubules to prepare membranes with positive, negative, and zero surface charge. As electroosmotic flow is directly related to surface charge the electroosmotic flow across the membrane varies accordingly. Finally, we have prepared poly(vinyl ferrocene) nanotubules conformally within the carbon nanotubules by electropolymerization. These polymeric nanotubules are electrochemically addressable. Reduction and oxidation of the poly(vinylferrocene) nanotubules effectively and reversibly turns electroosmotic flow on and off.

Conclusions: For the Biomolecular Division we have developed a method to prepare and characterize a "bilayer mimic" on the surface of our gold nanotube membranes. This "bilayer mimic" will serve as the host for the α -hemolysin channel. We have also begun experiments that will allow us to study the interaction of the α -hemolysin with this "bilayer mimic". Additionally, we have developed a simple and reliable method to isolate single pores in the nanotube membranes. For the Electrochemistry Division we have investigated transport as a function of electroosmotic flow for carbon nanotubule membranes. Additionally, we have studied the effects of transmembrane applied current, electrolyte pH and concentration, and carbon nanotubules modification on electroosmotic flow. Finally, we have demonstrated dynamic control of electroosmotic flow by using the carbon nanotubule membrane as an electrode to electrochemically vary the membrane surface charge. This is an important step in studying electroosmotic flow at the nanoscale.

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